

# XAFS Study of Nanocrystalline $\text{TiO}_2\text{-(MoO}_3)_x$ Core-Shell Materials

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## Introduction

There has been extensive research activity focused on the synthesis and photophysical property characterization of nanocrystalline  $\text{TiO}_2$  since the discovery that  $\text{TiO}_2$  could photoelectrolyze water to produce  $\text{H}_2$ . The stimulus behind this research is the potential for converting light to electrical energy (photovoltaics) or chemical energy (photocatalytic splitting of water, photooxidation of harmful organics and microorganisms) by solar-driven bandgap excitation of  $\text{TiO}_2$ . Additionally,  $\text{TiO}_2$  is inexpensive, non-toxic and water stable, which makes it amenable for use in a wide range of processes with minimal environmental impact. Unfortunately,  $\text{TiO}_2$  has physical property limitations with regard to its practical solar energy applications, most notably the bandgap energy (3.2 eV) is well outside the most intense region of the solar spectrum (centered at  $\sim 2.6$  eV). To this end, our research effort in this area is focused on the synthesis of new nanoarchitected metal oxide materials with photophysical properties that can potentially be tuned for practical solar energy conversion.

As an example, we discovered a series of nanoarchitected compounds composed of nanocrystalline anatase  $\text{TiO}_2$  and molybdenum oxide. We immediately observed that these materials exhibited both novel structural and electronic properties. First, we experimentally determined from X-ray powder diffraction (XRPD) experiments that the size of the nanocrystalline  $\text{TiO}_2$  particles could be adjusted from 80-40 Å by simply increasing the fraction of molybdenum oxide included in the syntheses. Second, these compositional and nanostructural changes were accompanied by dramatic optical property changes – as the  $\text{TiO}_2$  crystallite size decreased (and the molybdenum oxide content increased), the bandgap energy ( $E_g$ ) of these materials systematically decreased from 2.88 to 2.60 eV. This  $E_g$  red-shift trend is opposite of that predicted based on quantum size effects, and has never before been reported.

Our XRPD and high resolution transmission electron microscopy studies revealed that these materials were composed of nanocrystalline  $\text{TiO}_2$ , but we learned nothing about the structural nature of the molybdenum oxide. Yet, we knew that by understanding in detail the structural features of these nanomaterials, we could in turn have a better opportunity to fully describe their electronic properties. We therefore collected X-ray absorption near edge structure (XANES) data as a means to separately evaluate the Ti-O and Mo-O structural connectivity.

## Methods and Materials

Measurements were made at 20-ID-B during the beamline commissioning period. For the Mo edge, powder samples were contained in thin wall glass capillaries varying in diameter from 0.2 to 0.5 mm depending on the concentration. For the Mo standard powders and the Ti edge measurements, the samples

were rubbed onto adhesive tape. Typically, 4 layers of tape gave an absorption step of 1-1.5 for the Ti edge samples, and 8 layers sufficed for the Mo standards. Data was collected in both transmission and fluorescence mode, with the fluorescence signal used for the more dilute Mo samples.

## Results

The Ti K-edge and pre-edge data for all four  $\text{TiO}_2\text{-(MoO}_3)_x$  compounds were nearly identical to that of the  $\text{TiO}_2$  (anatase) standard. This supports the XRPD data and confirms that there was very little, if any, Mo in the anatase lattice – the  $\text{TiO}_2$  and molybdenum oxide are in separate phases with an interface.

Similarly, the Mo K-edge XANES data collected from these materials clearly demonstrated that the edge and pre-edge features were very much similar to those of bulk crystalline  $\alpha\text{-MoO}_3$ , again supporting the structural model that the nanocrystalline  $\text{TiO}_2$  and the molybdenum oxide were in separate and distinct phases. Some examples are shown in the Figure.

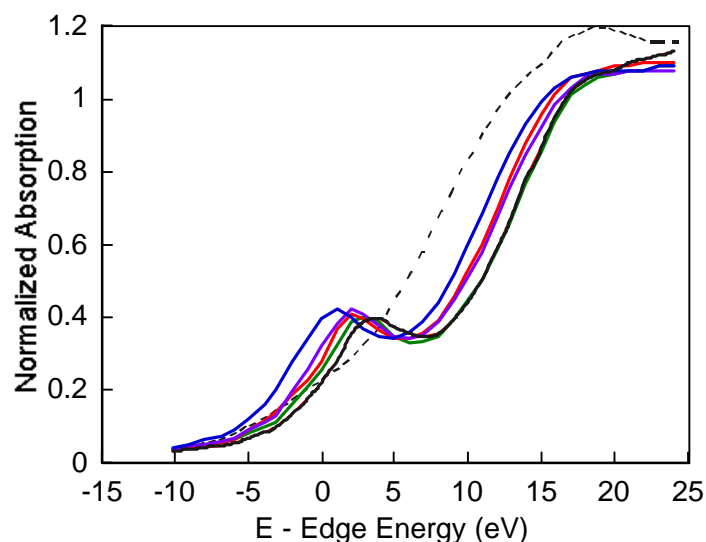


Figure 1: Mo K-edge results. Black lines are standards (solid- $\text{MoO}_3$ , dashed- $\text{MoO}_2$ ). The rest are  $\text{TiO}_2\text{-(MoO}_3)_x$  with  $x=0.04$  (green),  $x=0.17$  (red),  $x=0.38$  (magenta), and  $x=0.44$  (blue). The edges are all normalized and referenced to the edge of Mo metal.

## Discussion

There is a clear trend of the edge energy shifting to lower energy at the  $\text{MoO}_3$  content increases. The shift suggests O to Mo charge transfer (increasing covalency of the Mo-O bonds). The EXAFS, measurements at the Mo  $L_3$  edge, and chemical analysis indicate that the Mo remains in the  $6^+$  valence with a generally octahedral environment.

These XANES data, in conjunction with the other experimental evidence, provided us with the information to conclude that these materials were indeed nanoarchitected – a nanocrystalline TiO<sub>2</sub> core with an  $\alpha$ -MoO<sub>3</sub>-like shell. We then developed a model in which we were able to correlate the novel photophysical properties, taking into consideration the semiconductor nanoheterojunction at the core-shell interface, with the core-shell architecture.[1]

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### References

[1] S. H. Elder, F. M. Cot, Y. Su, Y. Gao, S. M. Heald, M. L. Balmer, and Ana C. Kolwaite, J. Am. Chem. Soc., in press.